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(71) Applicant (*for all designated States except US*): COGNITIVE SOLUTIONS LTD. [GB/GB]; 13 Herries Road, Pollokshields, Glasgow G41 4DE (GB).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*): McNAUGHTON, Moyra [GB/GB]; 276A Main Road, Elderslie, Johnstone PA5 9EF (GB).

(74) Agent: MURGITROYD & COMPANY; 373 Scotland Street, Glasgow G5 8QA (GB).

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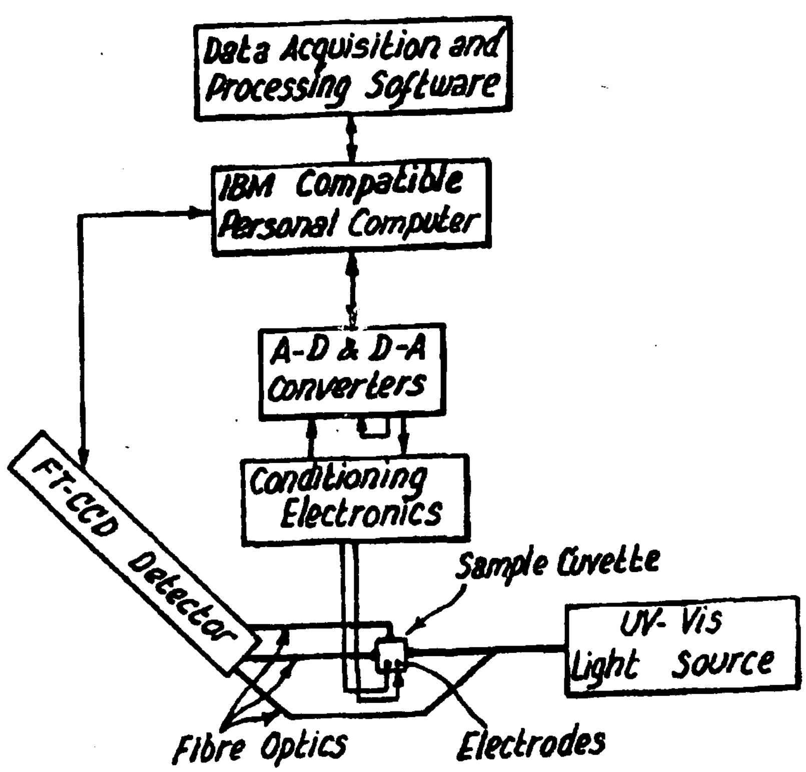
(54) Title: DETECTOR FOR CHEMICAL ANALYSIS

(57) Abstract

A tri-state detector which may be used for chemical analysis of flowing streams has a flow cell, light source, radiation detector and a micro-electrode chemical detector, the radiation detector being, for example, a Fourier Transform UV/visible spectrometer.



"Detector for Chemical Analysis"

This invention relates to detectors and particularly tri-state detectors for use in chemical analysis of flowing streams. Such streams may be found in industrial processes, trade effluents, clinical solutions, or environmental waters, and will contain ions and molecules with a range of chemical properties.

Process and environmental monitoring in the chemical industry is largely carried out in centralised laboratories which may be some distance away from where the sample is taken, resulting in a time delay between sampling and analysis. Should a fault develop in a manufacturing process, the time taken to detect the problem could be costly in terms of loss of production or damage to the environment. There is increasing need, therefore, in the chemical industry for the type of chemical detector that can be used on-line to give real-time chemical analysis of process or effluent streams, with the aim of improving product yield and quality whilst safeguarding the environment.

Current provision for the chemical analysis of these sample streams is usually capable of dealing with only

one chemical property at a time. Most molecules may be characterised by their absorption or emission of light, or their electrical activity. At present, the methods of UV/visible absorbence, fluorescence and electrochemical analysis are all commonly used, separately, for the determination of chemical species (the analyte) in solution. Each method of detection is required depending on the type and concentration of analyte present in the sample. For example, not all molecular species can be detected by UV or fluorescence methods so that an electrochemical method may be more suitable for that particular analyte. In order to carry out a complete conventional analysis of complex sample may therefore require that the analysis is repeated with each of these three techniques in turn, resulting in long analysis times. Three different instruments will also be required, with obvious cost implications. The amount of chemical information that each technique can provide on its own is limited, whereas the combination of the three techniques will provide more detailed information regarding a particular sample.

According to the first aspect, the present invention provides a detector which is adapted to simultaneously investigate the following properties of a sample:

a) absorbance with respect to electromagnetic radiation;

b) fluorescence and/or emission; and

c) electrochemical properties.

The sample is preferably a flowing stream. It may be, for example, a process or effluent stream, or an eluent from a chromatography column.

Absorbance of the sample is preferably investigated

with respect to ultra-violet and/or visible radiation.

The detector may be capable of multi-wavelength measurement or analysis. It may be provided with one or more rapid scanning monochromators. This may allow rapid wavelength scanning when the detector operates in an absorbance and/or an emission mode; this facilitates rapid acquisition of chemical information relating to the sample. The detector may comprise one or more solid state monochromators.

The electrochemical properties or activity of the sample may be determined using an amperometric or coulometric technique. Preferably, pulsed amperometric detection (PAD), which can detect any sample molecule which has the ability to undergo an oxidation or reduction reaction at an electrode and produce an electrical current is used. A potential applied to the electrode is chosen to match the oxidation or reduction potential of an analyte species; the amount of current generated is proportional to the analyte concentration.

The detector may utilise a single microelectrode to conduct electrochemical analysis; this may have a surface diameter of less than 100μm. Alternatively, an array of several microelectrodes may be used, each of which may be set to a different measurement potential to allow selective detection and concentration measurement of each electroactive species present. The detector may incorporate a de-mountable electrode unit. This may comprise a microelectrode or microelectrode array for use in electrochemical analysis. The electrode unit may be removable to facilitate cleaning and restoration of a surfac or surfaced of the electrode or electrodes; it may be disposable and this may alleviate probl ms of contamination of the

electrode surface or surfaces. A common problem with existing electrochemical detectors is that of contamination of the electrode surface leading to a loss in sensitivity.

According to a second aspect, the present invention provides a detector adapted to investigate electrochemical properties of a sample in which the detector comprises a removable electrode unit.

According to a third aspect, the present invention provides a detector adapted to investigate absorbance, fluorescence or emission of a sample in which the detector comprises one or more solid state monochromators.

According to a fourth aspect, the present invention provides a tri-state detector comprising a Fourier Transform UV/visible spectrometer.

An embodiment of the invention will now be described, by way of example only, with reference to the accompanying drawings of which:

Fig. 1 is a schematic perspective view of a detector;
Fig. 2 is a cross-section through Fig. 1; and
Fig. 3 is a schematic diagram of a tri-state detector.

The detector which is illustrated schematically in the accompanying drawings has the ability to carry out a detailed chemical analysis of a flowing stream. The detector is compact, easy to use and relatively low-cost in comparison with single-component detectors pr sently available. It is a tri-state detector. It incorporates appropriate optical components and is

intended for use with appropriate data-handling softwar .

Referring to the drawings, light from a polychromatic light source 3 irradiates the face of an optically transparent flow cell 4. A monochromator 10, placed between the source 3 and the flow cell 4 is used to select radiation of specified wavelengths and the absorbance of the radiation by the analyte present in solution is measured in the x-plane by a photomultiplier 11. This incident radiation also serves as the excitation source for the emission mode. Simultaneously, fluorescent emission is measured at right angles to the incident radiation via a second monochromator 12, which is used for the wavelength selection of the emitted radiation, with a second photomultiplier 13. An electrochemical detector 15, which in this embodiment is a microelectrode or microelectrode array, is incorporated with a de-mountable electrode unit in the floor of the flow-cell so as not to interfere with the light path, and measures current as a function of electrode potential as electroactive analyte species are oxidised at the electrode. The electrochemical unit can be easily removed from the flow cell for cleaning/restoration of the electrode surfaces. A personal computer (not shown) and appropriate software is used for data collection and analysis. The flow cell may be interfaced to an existing separation system (eg HPLC), or may be incorporated within the pipework of an industrial plant or used for effluent monitoring.

Advantages of this detector include the following features:-

(1) Three detection modes incorporated within one

device allow simultan ous absorbance/emission/electrochemical measurement of a wide variety of both organic and inorganic species.

(2) Use of an electrochemical detector with a single microelectrode or an array of several microelectrodes, each set to a different measurement potential, allows selective detection and concentration measurement of each electroactive species present.

(3) In one embodiment, the detector makes use of two rapid scanning monochromators, preferably acousto optic tunable filters, for selecting the wavelength of light from the source and also that emitted as fluorescent radiation from the sample. Use of these devices allows rapid scanning across the chosen wavelength region of the electromagnetic spectrum, so that measurement of absorbance or fluorescent emission is not restricted to one wavelength at a time.

(4) The electro-chemical detector may be fabricated as a de-mountable unit. This allows easy access to the electrodes for cleaning and helps to alleviate the well-known problems of electrode contamination.

(5) The de-mountable electrode unit may be disposable.

(6) Shorter analysis times and increased sample throughput for liquid chromatography.

(7) Reduced cost compared to that of separate detectors.

(8) Capabl of *in situ* r al-time measurement of process or effluent streams.

(9) Use of the specified monochromator allows rapid wavelength scanning and facilitates the rapid production of fluorescence/absorbance emission/excitation maps/ thus providing detailed chemical information regarding the analyte species.

(10) Use of solid state monochromators and microelectrodes provides a compact device with no mechanical moving parts.

(11) Use of state-of-the-art data acquisition software allows rapid data handling and storage.

Referring to Fig. 3, light from a polychromatic source irradiates the face of the optically transparent flow cell via a fibre optic connection. This light passes through the sample solution where it is absorbed by optically active analyte molecules. The incident radiation also serves as the excitation source for the flourescence mode. The absorbance of radiation in the x-plane and the fluorescent emission in the y-plane are measured by the Fourier Transform (FT) spectrometer, via a network of fibre optic connections and switching devices.

The electrochemical detector, which is a single microelectrode or microelectrode array, may be incorporated within a de-mountable unit in the body of the flow-cell so as not to interfere with the light path, or may comprise a unit immediat ly downstream of the optical flow c ll. It is anticipated that th microelectrod unit will be easily removed from the

flow c ll for cleaning or replacement, and can be made cheaply enough to b ssentially disposable.

The entire system is controlled from a PC; the software for data acquisition and processing via an on-board A/D and D/A card has been developed using National Instruments Labview and LabWindows. The control and information flow between the main software package and the FT spectrometer control software is via the Dynamic Data Exchange (DDE) facility of Microsoft Windows. Experimental parameters such as number of scans acquired, output waveform to the electrochemical detector and presentation of data are managed via a graphical user interface in the Windows environment.

Through the use of specified optical components and appropriate data-handling software, the device will be compact, easy to use and relatively low-cost in comparison with equivalent combinations of single-component detectors presently available. The advantages of this tri-state detector may be summarised as follows:-

- Three detection modes incorporated within one compact device.
- Simultaneous measurement of light absorption and emission together with electrochemical activity of molecular species.
- Shorter analysis times and increased sample through-put for liquid chromatography.
- Reduced cost compared to that of separate detectors.
- Capable of in-situ real-time measurement of process or effluent streams.
- Measurement of absorption and fluorescence can be achieved in circa 1ms, allowing fast rep titiv

scans in the situation where there is rapidly changing signal, (eg fast kinetic processes).

- An easy-to-use Windows interface provides user-transparent data acquisition and processing.
- The system can be used with existing liquid chromatographic equipment.
- The detector components may also be used as stand alone instruments: UV/visible absorption spectrometer, fluorescence spectrometer and electrochemical detectors, thus offering a higher degree of flexibility in the use of all or any of the component parts of the detector.
- Use of the FT Spectrometer, which is itself novel, ensures a compact device with no mechanical moving parts.
- Easily de-mountable unit containing the microelectrode will simplify the task of electrode cleaning or replacement.
- Information from the FT Spectrometer is available in digital form immediately with no hardware or software processing.
- Potential exists for a portable version to be used with a lap-top PC in combination with a battery powered detection system.

The proposed tri-state detector is unique in the use of a Fourier Transform UV/visible spectrometer, to provide a compact device which has the capability of multiwavelength measurement. Also innovative is the deign and fabrication of the de-mountable electrode unit, which may be disposable, to circumvent problems of contamination of the electrode surface.

Modifications and improvements may be incorporated without departing from the scop of the invention.

CLAIMS

1 A detector which is adapted to simultaneously investigate the following properties of a sample:
a) absorbance with respect to electromagnetic radiation;
b) fluorescence and/or emission; and
c) electrochemical properties.

2 A detector as claimed in Claim 1, wherein absorbance of the sample is preferably investigated with respect to ultra-violet and/or visible radiation.

3 A detector as claimed in Claim 1 or Claim 2 capable of muiti wavelength measurement or analysis.

4 A detector as claimed in any one of the preceding Claims provided with one or more rapid scanning monochromators.

5 A detector as claimed in Claim 4, wherein one or more of the monochromators are solid state monochromators.

6 A detector as claimed in any one of the preceding Claims adapted to use amperometric techniques for determining the electrochemical properties or activity of the sample.

7 A detector as claimed in any one of the preceding Claims, comprising a single microelectrode for conducting electrochemical analysis.

8 A detector as claimed in Claim 7 wherein th

single microelectrode has a surface diameter of less than 100μm.

9 A detector as claimed in any one of Claims 1-7 comprising an array of several microelectrodes, each being set to a different measurement potential to allow selective detection and concentration measurement of present electro-active species.

10 A detector adapted to investigate electrochemical properties of a sample in which the detector comprises a removable electrode unit.

11 A tri-state detector comprising a Fourier Transform UV/visible spectrometer.

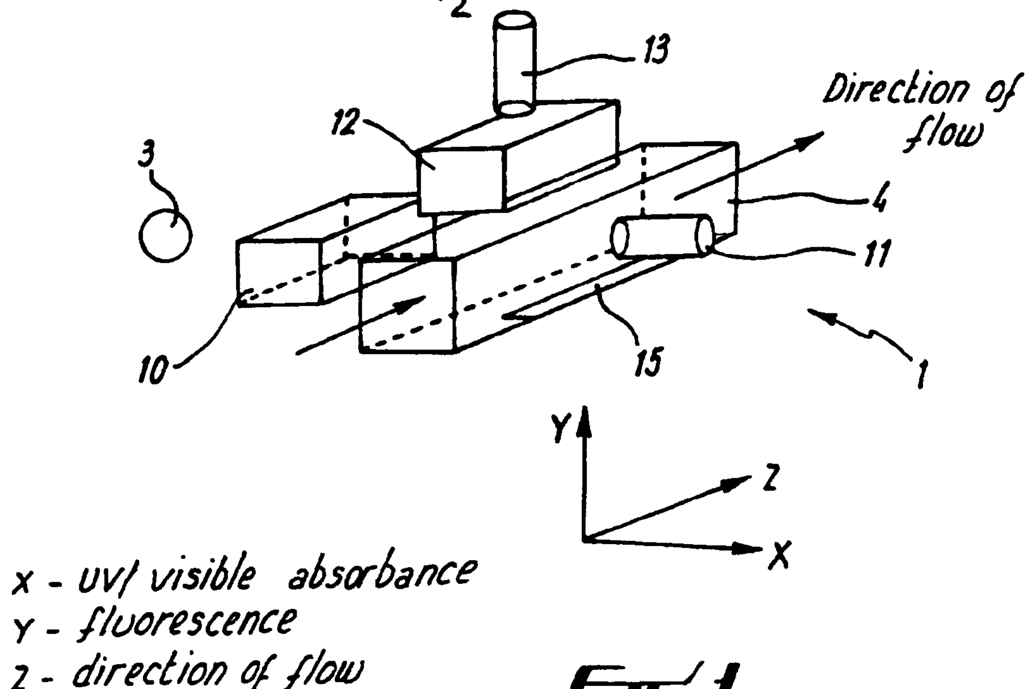

13
Direction of flow
12
3
4
11
10
15
1
Y
Z
X
x - UV/ visible absorbance
Y - fluorescence
Z - direction of flow

FIG. 1

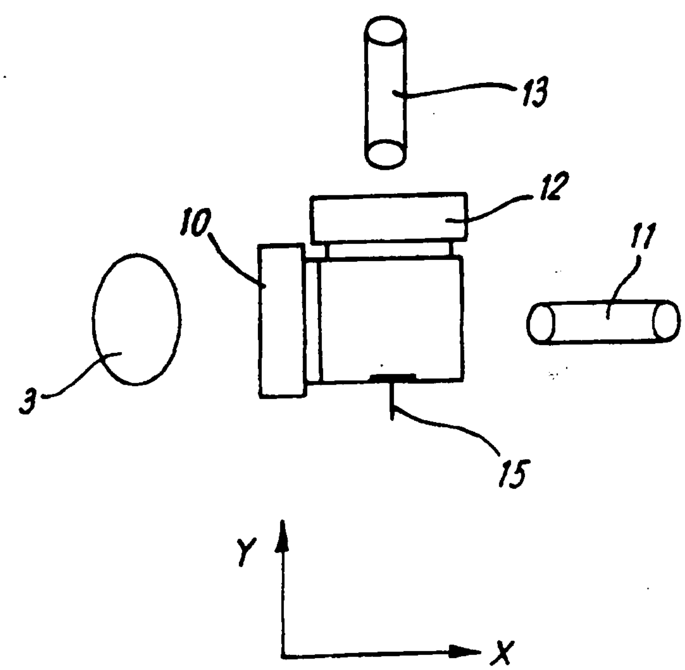

13
12
10
11
3
15
Y
X

FIG. 2

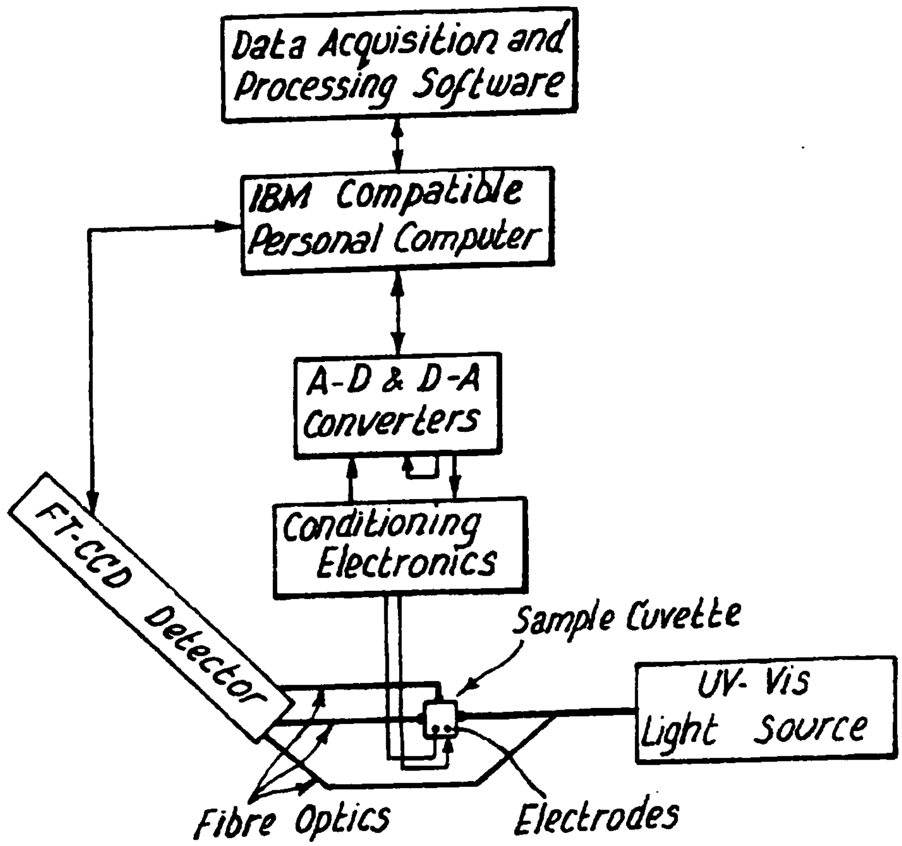

Data Acquisition and Processing Software
IBM Compatible Personal Computer
A-D & D-A Converters
Conditioning Electronics
FT-CCD Detector
Sample Cuvette
UV- Vis Light Source
Fibre Optics
Electrodes

FIG.3